

# STUDIES IN ADSORPTION

I—Adsorption From Aqueous Solutions by Silica  
II—Heat of Wetting of Carbon by Binary Liquid Mixtures

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements  
for the Degree of Doctor of Science in the University  
of Michigan.

By  
YING FU  
1928





# STUDIES IN ADSORPTION

I—Adsorption From Aqueous Solutions by Silica

II—Heat of Wetting of Carbon by Binary Liquid Mixtures

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements  
for the Degree of Doctor of Science in the University  
of Michigan.

By

YING FU

1928



\* 21004

#### ACKNOWLEDGMENT

These investigations were undertaken at the suggestion of Professor F. E. Bartell, for whose constant encouragement and advice the author wishes to express his gratitude.

He also wishes to thank Dr. Lee Su and Mr. C. K. Sloan for many suggestions.



## CONTENTS

### I. ADSORPTION FROM AQUEOUS SOLUTIONS BY SILICA

|                                              |    |
|----------------------------------------------|----|
| Introduction . . . . .                       | I  |
| Method of Preparation of Silica . . . . .    | 2  |
| Method of Conducting Experiments . . . . .   | 3  |
| Results of Experiments . . . . .             | 3  |
| Adsorption of Bases . . . . .                | 3  |
| Adsorption of Inorganic Acids . . . . .      | 4  |
| Adsorption of Organic Acids . . . . .        | 4  |
| Hydrolytic Adsorption . . . . .              | 6  |
| Influence of Solvent on Adsorption . . . . . | 9  |
| Summary . . . . .                            | 11 |

### II. HEAT OF WETTING OF CARBON BY BINARY MIXTURES

|                        |    |
|------------------------|----|
| Introduction . . . . . | 13 |
| Experimental . . . . . | 16 |
| Discussion . . . . .   | 19 |
| Summary . . . . .      | 23 |



Digitized by the Internet Archive  
in 2026

## ADSORPTION FROM AQUEOUS SOLUTIONS BY SILICA

Although a great amount of work has been done with both carbon and silica as adsorbents, the results reported by different investigators have been conflicting and satisfactory generalizations have been lacking. Bartell and E. J. Miller,<sup>1</sup> working on the assumption that many of the anomalies reported in the literature are due to the impurities in the adsorbents used, undertook the preparation of an ash-free active carbon. Exact methods of experimentation were observed and the results obtained with pure carbon appear to be free from anomalies. In view of the success of this work, it was thought desirable to make a similar study of adsorption with silica.<sup>2</sup>

It is well known that carbon exhibits a higher degree of adsorption from aqueous solutions than from solutions of organic liquids. Patrick and co-workers<sup>3</sup> have shown that silica adsorbs best from organic liquids. Work which has been carried out in this laboratory,<sup>4</sup> on adhesion tension of liquids against solids, has shown definitely that carbon has a high adhesion tension against organic liquids and a comparatively low adhesion tension against water. The order of adhesion tension of silica against these liquids is the opposite. In general, it can be stated that a liquid which exhibits a high adhesion tension against carbon will show a low adhesion tension against silica and vice versa. Other factors being equal, adsorption should be greatest from those solvents which have the lowest adhesion tension against the solid. It should, accordingly, follow that adsorption effects obtained with silica as an adsorbent should be very different, in fact, practically opposite to those obtained with carbon as adsorbent.

An extensive investigation on the adsorptive properties of hydrated silica has been carried out by Patrick and his co-workers.<sup>5</sup> They have studied the adsorption of gases, of vapors, of NaOH from solutions, and adsorption

\* The material presented in this paper is from a dissertation submitted by Ying Fu to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Science, 1928.

<sup>1</sup> J. Am. Chem. Soc., **44**, 1866 (1922); **45**, 1106 (1923).

<sup>2</sup> No attempt has been made to present a complete bibliography covering investigations on adsorption with silica and silica gel. Such a bibliography would include the classical researches of van Bemmelen and also the researches of many others. The work of this paper is most closely related to that indicated by the references cited herein.

<sup>3</sup> Patrick and Jones: J. Phys. Chem., **29**, 1 (1925).

<sup>4</sup> Bartell and Osterhof: Ind. Eng. Chem., **19**, 1277 (1927); Z. physik. Chem. Cohen-Festband, **130**, 715 (1927); "Colloid Symposium Monograph," **5** (1927); Bartell and F. L. Miller: Ind. Eng. Chem., **20**, 738 (1928).

<sup>5</sup> Patrick: Diss. Göttingen (1914); McGavack and Patrick: J. Am. Chem. Soc., **42**, 946 (1920); Patrick and Jones: J. Phys. Chem., **29**, 1 (1925); Patrick and Grimm: J. Am. Chem. Soc., **43**, 2144 (1921); Patrick and Barclay: J. Phys. Chem., **29**, 1400; Patrick and Eberman: 220; Patrick and Greider: 1031; Patrick and Long: 336; Patrick and Opdyke: 601; Patrick, Preston and Owens: 421 (1925); Patrick and Neuganssen: J. Am. Chem. Soc., **43**, 1844 (1921).



from organic liquids. They have also studied heat of wetting and heat of adsorption with silica, as well as the displacement of water from the hydrogel by other liquids. The latter was also studied by Firth and Purse<sup>1</sup> who concluded that water can be completely displaced from the gel by alcohol. This was not in agreement with Patrick's results. The most active gel recorded was that of Holmes and Anderson<sup>2</sup> and Holmes, Sullivan and Metcalf<sup>3</sup> who precipitated the silica gel from water glass solution by adding an excess of dilute solution of nickel or iron salts. The salts were removed with hydrochloric acid after the gel had been dried slowly at a low temperature. Adsorption with quartz and with silica which had been ignited for a long time were studied by Jones<sup>4</sup> and Joseph and Hancock.<sup>5</sup> Silica gel containing about 85% water has been used in adsorption studies by Mukherjee and his co-workers.<sup>6</sup>

### Method of Preparation of Silica

In nearly all previous investigations hydrated silica gel has been used in preference to the dehydrated gel or silica because of its greater activity. The method of preparing the gel has been essentially that used by MacGavack and Patrick.<sup>7</sup> Silicic acid is precipitated from water glass by the addition of hydrochloric acid and then is washed to remove the electrolytes. In the present investigation silica gel was at first prepared by this method and was partially dehydrated by heating. This treatment gave a very active gel, but the method was unsatisfactory, in that acid was left which was very difficult to remove without affecting the activity of the gel. It was found also that this gel was usually contaminated with a trace of sodium salt which, while not affecting the activity of the gel for the adsorption of gases, was undesirable for work on hydrolytic adsorption of salts. After trial of many methods, the method of Ebler and Felner<sup>8</sup> was finally adopted. Pure silicon tetrachloride was distilled into conductivity water surrounded by cracked ice until the resulting solution showed a slight blue tinge. The solution usually set to a gel within one hour. The gel was heated at a low temperature, about 60° C, to remove the major portion of the acid and the water. It was then transferred to quartz crucibles and heated in an electric oven at 260° C for two hours. Without being cooled down to room temperature the gel was taken out of the oven and immediately poured into warm conductivity water. After three or four washings by decantation, the gel was again placed in the oven at 260° C. Practically all the acid on the gel was removed by the first treatment, but the process was repeated at least six times to insure complete removal of impurities. Analysis showed that this silica contained no chloride and when

<sup>1</sup> J. Phys. Chem., 30, 617 (1926).

<sup>2</sup> Ind. Eng. Chem., 17, 280 (1925).

<sup>3</sup> Holmes, Sullivan and Metcalf: Ind. Eng. Chem., 18, 386 (1926).

<sup>4</sup> J. Phys. Chem., 29, 326, 369 (1925).

<sup>5</sup> J. Chem. Soc., 123, 2022 (1923).

<sup>6</sup> Mukherjee, Krishnamurti, Ghosh, Nutza and Roy: J. Chem. Soc., 128, 3023 (1926).

<sup>7</sup> MacGavack and Patrick: J. Am. Chem. Soc., 42, 946 (1920).

<sup>8</sup> Ber., 44, 1915 (1911).



treated with hydrofluoric acid left no residue. The silica gel thus prepared was slowly dehydrated until the water content was reduced to about four per cent, after which it was further dehydrated by heating with a blast lamp. With experience it became possible to reduce the silica to a condition of constant weight at the same time avoiding prolonged heating which would tend to decrease its adsorbing capacity. A quantity of such gel was prepared so that uniform samples might be used throughout the work.

### Method of conducting Experiments

The amount of adsorption was determined as follows. A definite quantity of solution, 40 cc., was placed in a glass-stoppered flask previously filled with  $\text{CO}_2$  free air, and an accurately weighed amount of silica, 0.6 to 0.8 gram, was added. After four hours of shaking the change in concentration of solution was determined by titration, care being taken to eliminate carbon dioxide in every titration. The amounts of adsorption, represented by  $x/m$ , (expressed in miligram-equivalents per gram of silica) in the tables are admittedly not strictly accurate in as much as no attempt was made to correct for the adsorption of solvent nor for the volume change due to adsorption of the solute. An error was undoubtedly introduced, but it must be very small as the volume change was small, and the solutions were so dilute that the adsorption of the solvent would not alter the bulk liquid concentration materially.

### Results of Experiments

*Adsorption of Bases.* The lithium hydroxide solution was prepared from lithium sulphate and barium hydroxide according to Harned's method.<sup>1</sup> The other bases were of C.P. quality. After treatment with silica as above described a portion of the liquid was pipetted off and titrated with bromthymol blue as indicator. All experiments were run in duplicate. The data given in Table I are averages of at least four independent determinations.

TABLE I

#### Adsorption of Inorganic Bases by Silica

| Base | Equil. Conc. | $x/m$ | Base                   | Equil. Conc. | $x/m$ |
|------|--------------|-------|------------------------|--------------|-------|
| LiOH | 0.0502 N     | 1.93  | KOH                    | 0.0631 N     | 1.55  |
|      | 0.0245 N     | 1.58  |                        | 0.0345 N     | 1.32  |
|      | 0.0100 N     | 1.24  |                        | 0.0159 N     | 1.06  |
|      | 0.0040 N     | 0.97  |                        | 0.0090 N     | 0.91  |
|      | 0.0025 N     | 0.85  |                        | 0.0049 N     | 0.75  |
| NaOH | 0.0630 N     | 1.70  | $\text{NH}_4\text{OH}$ | 0.0760 N     | 1.23  |
|      | 0.0338 N     | 1.38  |                        | 0.0298 N     | 0.85  |
|      | 0.0199 N     | 1.12  |                        | 0.0191 N     | 0.71  |
|      | 0.0100 N     | 0.90  |                        | 0.0112 N     | 0.60  |
|      | 0.0040 N     | 0.66  |                        | 0.0045 N     | 0.39  |

<sup>1</sup> J. Am. Chem. Soc., 48, 127 (1926).

The data plotted with  $x/m$  and equilibrium concentration values as co-ordinates are given in the curves in Fig. 1. It will be noted that typical adsorption isotherms are obtained. This indicates that adsorption or surface reactions must predominate. It seems probable that in these systems "chemical reactions" may and probably do occur, but they are limited to the surface only. In effect then these reactions are adsorptions of the "heteropolar" type which have been discussed by Freundlich and others. With the fairly dilute solutions used there appears to be no reason to consider the process to be other than one of adsorption.

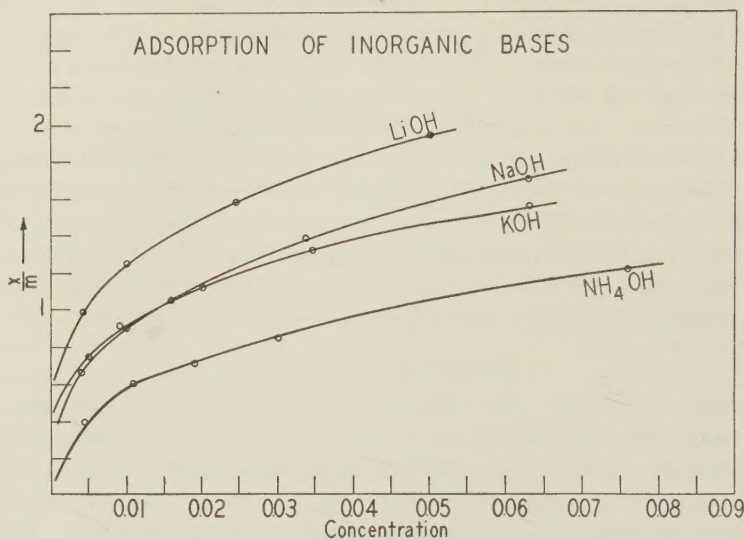


FIG. 1

### Adsorption of Acids

*Inorganic acids.* The hydrochloric acid used was constant boiling acid diluted with conductivity water. Nitric acid, sulphuric acid and perchloric acid were of C.P. quality. The results obtained with these acids are given in Table II.

TABLE II

#### Adsorption of Inorganic Acids by Silica

| Acid         | Equil. Conc. | $x/m$ | Acid       | Equil. Conc. | $x/m$ |
|--------------|--------------|-------|------------|--------------|-------|
| Hydrochloric | 0.0103 N     | 0.000 | Sulfuric   | 0.0101 N     | 0.000 |
| Hydrochloric | 0.1052 N     | 0.000 | Sulfuric   | 0.1000 N     | 0.002 |
| Nitric       | 0.0096 N     | 0.000 | Perchloric | 0.0084 N     | 0.000 |
| Nitric       | 0.0987 N     | 0.000 | Perchloric | 0.0913 N     | 0.000 |

The results show that none of these inorganic acids (i.e. within the range of the limits of experimental error) are adsorbed. This is contrary to the



results of Mukherjee and co-workers who used a gel containing about 85% water. The difference in results may be due to the water content of their gel.

#### ORGANIC ACIDS

All the organic acids used were purified by standard methods. Subsequent treatment was as above described. The results obtained with these acids are given in Table III.

TABLE III  
Adsorption of Organic Acids by Silica

| Acid      | Equil. Conc. | x/m   | Acid      | Equil. Conc. | x/m   |
|-----------|--------------|-------|-----------|--------------|-------|
| Formic    | 0.0100 N     | 0.009 | Succinic  | 0.0100 N     | 0.007 |
| Formic    | 0.0994 N     | 0.010 | Succinic  | 0.0316 N     | 0.008 |
| Acetic    | 0.0099 N     | 0.006 | Tartaric  | 0.0125 N     | 0.002 |
| Acetic    | 0.0410 N     | 0.006 | Tartaric  | 0.0892 N     | 0.004 |
| Propionic | 0.0104 N     | 0.007 | Lactic    | 0.1038 N     | 0.004 |
| Propionic | 0.0548 N     | 0.006 | Oxalic    | 0.0101 N     | 0.000 |
| Butyric   | 0.0099 N     | 0.005 | Oxalic    | 0.1064 N     | 0.000 |
| Butyric   | 0.0503 N     | 0.006 | Benzoic   | 0.0103 N     | 0.053 |
|           |              |       | Benzoic   | 0.0216 N     | 0.053 |
|           |              |       | Salicylic | 0.0088 N     | 0.053 |
|           |              |       | Salicylic | 0.0165 N     | 0.06  |

TABLE IIIa

#### Adsorption of Fatty Acids by Silica from Carbontetrachloride

| Equil. Conc. | x/m in millimole<br>per gram SiO <sub>2</sub> | Equil. Conc.   | x/m in millimole<br>per gram SiO <sub>2</sub> |
|--------------|-----------------------------------------------|----------------|-----------------------------------------------|
| Formic Acid  |                                               | Propionic Acid |                                               |
| 0.0158 N     | 1.35                                          | 0.0135         | 1.07                                          |
| 0.0339       | 1.55                                          | 0.0309         | 1.22                                          |
| 0.0911       | 1.90                                          | 0.0500         | 1.30                                          |
| 0.2187       | 2.29                                          | 0.0890         | 1.41                                          |
| 0.5248       | 2.72                                          | 0.2779         | 1.70                                          |
|              |                                               | 0.5010         | 1.82                                          |
| Acetic Acid  |                                               | Butyric Acid   |                                               |
| 0.0204       | 1.24                                          | 0.0144         | 1.03                                          |
| 0.0347       | 1.36                                          | 0.0393         | 1.16                                          |
| 0.100        | 1.66                                          | 0.0740         | 1.26                                          |
| 0.2771       | 2.00                                          | 0.162          | 1.38                                          |
| 0.5502       | 2.24                                          | 0.251          | 1.43                                          |
|              |                                               | 0.4025         | 1.53                                          |

It will be noted that all the organic acids with the exception of oxalic, appear to be slightly adsorbed by the silica. The greatest adsorption was obtained with salicylic and benzoic acids. These latter effects are not surprising since these acids are but slightly soluble in water.<sup>1</sup>

The fact that acids are so slightly adsorbed by silica from aqueous solutions does not imply that acids are not adsorbed by silica. The slight adsorption is due to the effect of the solvent used. If, instead of water, some organic liquid is used as solvent, quite different results will be obtained. Inasmuch as a fuller account of work of this type will be given in another paper, only one series, the adsorption of fatty acids from carbontetrachloride, is presented here.

With carbon as adsorbent the adsorption of the fatty acids from aqueous solutions increases regularly as we ascend the homologous series. From the above data it is noted that the order of adsorption of fatty acids by silica is just opposite to that by carbon, i.e. the adsorption of these acids decreases as we ascend the homologous series. The order of surface tension lowering of the aqueous solutions of these acids is in the order of increasing molecular weights. This is the same as the order of interfacial tension lowering of these solutions against carbon but opposite to the interfacial tension lowering against silica. Apparently there is no relation between the adsorbability of these acids with silica and the surface tension lowering of the solution. Further, it is evident that Traube's rule as ordinarily stated<sup>2</sup> cannot be applied to adsorption with silica. This fact has also been noted by Holmes and McKelvey.<sup>3</sup>

#### HYDROLYTIC ADSORPTION

From the work of Bartell and E. J. Miller<sup>4</sup>, Miller<sup>5</sup> and Kolthoff<sup>6</sup> with ash free carbon, it has been shown that carbon, properly prepared, adsorbs acids, both organic and inorganic, but does not adsorb inorganic bases. On the other hand, silica, freed from impurities, as used in this work, was found to adsorb inorganic bases, organic acids slightly, but the inorganic acids not at all. Within the range of concentration studied, from 0.1 N to 0.001 N, the Freundlich equation was found to hold for adsorption of bases within the limit of experimental error.

It was observed by Bartell and Miller<sup>7</sup> and was conclusively proven later by Miller<sup>8</sup> that a large number of neutral salts, inorganic as well as organic,

<sup>1</sup> The results obtained with hydrated silica, containing 4 per cent. water, showed that the total adsorption with bases was considerably greater than with anhydrous silica, with organic acids somewhat greater, but in all cases the order of adsorption was the same as given above. The greater adsorption was probably due to the larger surface area of the hydrated silica, as will be shown in a later paper.

<sup>2</sup> Freundlich: "Colloid and Capillary Chemistry," 195.

<sup>3</sup> J. Phys. Chem., **32**, 1522 (1928).

<sup>4</sup> J. Am. Chem. Soc., **44**, 1866 (1923); **45**, 1106 (1923).

<sup>5</sup> J. Phys. Chem., **30**, 1162, 1031 (1926); J. Am. Chem. Soc., **47**, 1270 (1925).

<sup>6</sup> Rev. Trav. chim. Pays-Bas, **46**, 549 (1927).

<sup>7</sup> J. Am. Chem. Soc., **44**, 1866 (1922); **45**, 1106 (1923).

<sup>8</sup> J. Am. Chem. Soc., **46**, 1150 (1924).



were hydrolytically adsorbed by pure carbon. This follows from the fact that carbon adsorbs the acid preferentially and leaves the basic constituent in the solution. Since silica adsorbs base preferentially, it might be expected that hydrolytic adsorption would likewise occur with this adsorbent with salt solutions, the difference between carbon and silica adsorptions being that in the latter case, it would be the acid instead of base which would be split off and left in solution. This was found to be the case, as is shown by Table IV.

TABLE IV  
Hydrolytic Adsorption of Alkali Salts by Pure Silica

| Salt<br>(40 cc. solution) | 0.01N Acid set<br>free by 1 gm SiO <sub>2</sub> | Salt                                | 0.01N Acid set<br>free by 1 gm SiO <sub>2</sub> |
|---------------------------|-------------------------------------------------|-------------------------------------|-------------------------------------------------|
| Na formate .05 N          | 2.64 cc.                                        | NaCl 2 N                            | 1.88 cc.                                        |
| Na acetate .05 N          | 4.94 cc.                                        | NaNO <sub>3</sub> 2 N               | 1.84 cc.                                        |
| Na propionate .05 N       | 5.13 cc.                                        | NaClO <sub>3</sub> 2 N              | 1.75 cc.                                        |
| Na butyrate .05 N         | 5.20 cc.                                        | Na <sub>2</sub> SO <sub>4</sub> N/4 | 0.25 cc.                                        |
|                           |                                                 | KCl 2 N                             | 1.60 cc.                                        |
| Na tartrate .05 N         | 3.22 cc.                                        | LiCl 2 N                            | 2.03 cc.                                        |
| Na benzoate .05 N         | 3.91 cc.                                        |                                     |                                                 |
| Na oxalate .05 N          | 2.20 cc.                                        |                                     |                                                 |
| Na salicylate .05 N       | 1.26 cc.                                        |                                     |                                                 |

Even though inorganic bases are readily adsorbed and the inorganic acids are not, their salts are apparently but slightly hydrolysed during the adsorption by silica. In the case of 0.02 N solutions the pH value of the solution was in some experiments found to change from 7.0 to 5.2 for the alkali salts of strong inorganic acids. The acid thus liberated is in such small quantity that it can scarcely be titrated with a base. In the case of solutions of salts of the organic acids, the acids of which are adsorbed to a greater extent than the inorganic acids, the results at first thought appear to be inconsistent for the hydrolysis is comparatively high. With 40 cc. of the 0.05 N solutions the acids liberated were in some cases equivalent to about 5 cc. of 0.01 N NaOH. The above results do not appear, to be in agreement with those of Bartell and Miller with carbon. In their work it was shown that the amount of base liberated by carbon was in the same order as the adsorbability of the acids with which the cation was combined. This apparent discrepancy, however, can be explained from the following consideration. Since but a small amount of acid was liberated from the inorganic salts, there must have been an equilibrium involving adsorption and de-sorption of the base, which greatly limited the amount of base which could be held by the silica: Had this not been the case the adsorption of the base would have proceeded to such an extent that a large amount of free acid would have been left in the solution. When acids are liberated, they tend to neutralize the adsorbed bases in a manner according to the strength and adsorbability of the acids. The stronger the acids the more base on the silica surface will be neutralized by them. Since organic acids, as a rule, are weaker than inorganic acids, they

are not so effective in the removal of the adsorbed base: hence more hydrolysis will occur. In order to test the above assumption, the following experiment was carried out.

After the silica had been treated with NaOH, the solution of base was poured off and the silica was rinsed twice with conductivity water; twenty-five cc. were used each time. The total amount of base adsorbed was determined by titrating the solution poured off, including also the rinsing water. The amount of water adhering to the silica after rinsing was determined by weighing. Since the amount of base adsorbed by the silica was known, the quantity of water adhering to the silica surface could be determined. A definite volume of different acids (40 cc.) of approximately equal concentration, was then added to the silica and after four hours of shaking the amount of acid neutralized by the adsorbed base was determined. In this manner it was found that inorganic acids removed all the adsorbed base while the organic acids always left some base on the silica even though the acid present was more than necessary to neutralize the base.

TABLE V  
Displacement of the Adsorbed NaOH by Different Acids

| Acid (40 cc.) | .01N NaOH on<br>SiO <sub>2</sub> | Acid taken up<br>by SiO <sub>2</sub> | NaOH left on<br>SiO <sub>2</sub> |
|---------------|----------------------------------|--------------------------------------|----------------------------------|
| Hydrochloric  | 29.50 cc.                        | 29.47 cc.                            | 0.03 cc.                         |
| Nitric        | 29.43 cc.                        | 29.43 cc.                            | 0.00 cc.                         |
| Formic        | 29.40 cc.                        | 28.00 cc.                            | 1.40 cc.                         |
| Acetic        | 30.00 cc.                        | 27.40 cc.                            | 2.60 cc.                         |
| Propionic     | 29.40 cc.                        | 26.80 cc.                            | 2.60 cc.                         |
| Butyric       | 29.70 cc.                        | 27.00 cc.                            | 2.70 cc.                         |
| Benzoic       | 29.12 cc.                        | 27.40 cc.                            | 1.72 cc.                         |
| Oxalic        | 29.32 cc.                        | 27.00 cc.                            | 1.32 cc.                         |
| Salicylic     | 29.24 cc.                        | 28.30 cc.                            | 1.04 cc.                         |

From Table V it is seen that the order in which the acids displace the base is just the reverse of the order of the increasing hydrolytic adsorption of their salts. It is also shown that the stronger the acid the more base it will displace. An exception to the last statement is given with salicylic acid which, aside from the inorganic acids, displaced the largest amount of base. If, however, we consider the adsorbability of the different acids, this apparent anomaly disappears, because it was found that salicylic acid is the most highly adsorbed acid among those used.

In his investigation on the adsorption of inorganic salts by carbon, Miller<sup>1</sup> found the adsorption to be purely hydrolytic in nature. None of the salt as such was adsorbed. In this investigation we wished to determine whether the adsorption of neutral salts by silica is also purely hydrolytic. In order to determine this, titration of the acid set free is alone not sufficient, both

<sup>1</sup> J. Am. Chem. Soc., 46, 1150 (1924).



molecular and hydrolytic adsorption might occur simultaneously and not be differentiated by the titration. It is, therefore, necessary to determine the concentration of the cation and of the anion both before and after the adsorption, in addition to the determination of the free acid present in the solution. If the process be exclusively hydrolytic, the concentration of the cation in solution should decrease in proportion to the increase in acidity of the solution, while the concentration of the anion should remain constant: if, on the other hand, the adsorption be both molecular and hydrolytic, no such proportionality would be found. To test this point 40 cc. of solution of KCl (approximately 1 N) were treated with about three grams of pure silica and the concentrations of both the cation and anion were determined. The potassium was determined by Smith's perchlorate method<sup>1</sup> and the chloride was determined with silver nitrate volumetrically. The results obtained follow: Before adsorption

10 cc. of the KCl solution required 21.06 cc.  $\text{AgNO}_3$  (0.50 N)  
 20 cc. of solution gave 2.9138 gms.  $\text{KClO}_4$   
 Solution was neutral.

After adsorption

10 cc. of the solution required 21.07 cc.  $\text{AgNO}_3$   
 20 cc. of solution gave 2.9118 gms.  $\text{KClO}_4$   
 3.30 cc. acid (0.01 N) was set free.

Altogether four samples were used, and similar results were obtained in each case. The discrepancy in the different determinations was well within the limits of accuracy of the method. The amount of hydrochloric acid set free was equivalent to 0.0045 gm. of  $\text{KClO}_4$ , while the decrease in potassium determined by the perchlorate method was equivalent to 0.0040 grams  $\text{KClO}_4$  (average of four determinations). The concentration of the cation, K, in solution was thus shown to decrease during adsorption by an amount equivalent to the increase in acidity of the solution. The concentration of the Cl ion was shown to remain unchanged. The adsorption of KCl by silica was, then, completely hydrolytic and no KCl as such was adsorbed.

#### INFLUENCE OF SOLVENT ON ADSORPTION

It is well known that a solvent has a marked influence on adsorption. Different theories have been advanced to account for this influence, but none of them seem to be sufficiently comprehensive. In developing a general theory, one must consider not only the influence of the solvent on the adsorbate, but also its influence on the adsorbent. The first factor is determined by the solubility of the solute and the second factor by the adhesion tension of the solvent against the adsorbent. When an adsorbent is added to a solution, an equilibrium is soon set up between the adsorbed and the unadsorbed portions of the solute. The amount of the solute that will be

<sup>1</sup> J. Am. Chem. Soc., 47, 762, 774, 1020 (1925).

adsorbed depends first of all on its chemical potential. The relation between solubility and chemical potential has been expressed by W. Lash Miller<sup>1</sup> as follows:

"If the solution of the substance S be prepared of equal concentrations in different solvents, the potential will be greatest for that solution which is nearly saturated; or the greater the solubility of S in any solvent the less the potential for any given concentration." The inverse relation between adsorption and solubility has been emphasized by Patrick and Jones who stated that "no exception has been found to the generalization that greater adsorption always follows lower solubility of the solute adsorbed in the solvent." This statement is also supported by our data from which the following two examples are chosen.

TABLE VI  
Adsorption of Benzoic Acid by Silica

| From carbon tetrachloride |      | From benzene |       |
|---------------------------|------|--------------|-------|
| Equil conc.               | x/m  | Equil conc.  | x/m   |
| 0.0383 N                  | 0.75 | 0.0400 N     | 0.371 |
| 0.0766 N                  | 1.03 | 0.0470 N     | 0.405 |
| 0.1169 N                  | 1.34 | 0.120 N      | 0.57  |
| 0.2529 N                  | 1.95 | 0.196 N      | 0.67  |

The solubilities of benzoic acid in carbon tetrachloride and in benzene are 4.18 and 12.43 respectively at 25°.

The above theory, thermodynamically sound as it is, is not sufficient to account for all the facts observed, as for example, Freundlich<sup>2</sup> found that from different solutions of the same concentration carbon adsorbs the same amount of benzoic acid from benzene as from ether, even though the solubilities of the acid in these liquids are 12 and 46 grams respectively. The insufficiency of the solubility relationship is also shown from the familiar fact of removing the adsorbed benzoic acid from carbon by washing the solid with organic liquids. In this case benzene was found to be more efficient in the removal of adsorbed benzoic acid than alcohol even though the latter can dissolve much more of the acid than benzene. This anomaly must be explained by considering the influence of the solvent on the adsorbent.

If the solvent has a high interfacial tension against the solid, it is then possible to cause a marked depression of this tension by adding a solute, thereby a high adsorption will occur. The high adsorption from water is generally explained in this way. Thus Freundlich<sup>3</sup> stated: "Water is characterized by a high surface tension and by a high interfacial tension against other liquids. We may therefore ascribe to it also a high interfacial tension against solids, especially hydrophobic solids. On the other hand, adsorption is low from organic liquids such as benzene, alcohol, etc., in the case of which we may assume for similar reasons a low interfacial tension against solids."

<sup>1</sup> J. Phys. Chem., **1**, 653 (1897).

<sup>2</sup> Z. physik. Chem., **57**, 385 (1907).

<sup>3</sup> "Colloid and Capillary Chemistry," 192.



The above generalization does not hold for silica and probably would not hold for other hydrophilic solids. Bartell and Osterhof<sup>1</sup> have shown in their investigation on the adhesion tension of liquids against carbon and silica that while organic liquids have, in general, a low interfacial tension against carbon, they have a high interfacial tension against silica. Therefore silica should adsorb best from organic solvents. For examples, from solutions of the same concentration, with water and carbon tetrachloride as solvents, silica was found to adsorb 0.05 and 0.32 millimoles of benzoic acid respectively.

In order to compare the influence of solubility on adsorption, it is important to use solvents which have the same interfacial tension against the adsorbents. Since, as has been shown in this laboratory, benzene and carbon tetrachloride have approximately the same adhesion tension against silica, it must follow that the interfacial tension against silica must be similar, therefore one is justified in comparing results obtained with these two liquids. If one wishes to study the relation between adhesion tension of the solvent against the solid and the degree of adsorption, it is necessary to use adsorbates which have the same solubility in the solvents in question. In general, we may say that if the solubility of the adsorbate is the same in different solvents, greater adsorption will occur from solutions the solvent of which has a lower adhesion tension against the solid. On the other hand, if the adhesion tensions of the solvents are the same, then greater adsorption will occur from those solvents in which the adsorbate is less soluble.

### Summary

1. Hydrolytic adsorption occurs when aqueous salt solutions are treated with pure dehydrated silica prepared from silicon tetrachloride. The basic constituent is preferentially adsorbed from such solutions. In general, bases are adsorbed, organic acids are slightly adsorbed and inorganic acids are not adsorbed at all.

2. Inorganic bases are preferentially adsorbed in the order  $\text{LiOH} > \text{NaOH} > \text{KOH} > \text{NH}_4\text{OH}$ . This order is the same as that for the degree of hydration of the cations. The order of adsorption is probably due to the strongly hydrophilic nature of the silica.

3. Organic acids are adsorbed in decreasing amounts in an ascending homologous series, i.e.,  $\text{Formic} > \text{Acetic} > \text{Propionic} > \text{Butyric}$ . This order is more pronounced in adsorption from organic solvents.

4. From solutions of sodium salts of the organic acids hydrolytic adsorption (preferential adsorption of base) occurs in increasing amounts in the ascending homologous series, i. e.,  $\text{Na formate} < \text{Na acetate} < \text{Na propionate} < \text{Na butyrate}$ .

5. Inasmuch as an equilibrium condition exists between the base adsorbed and the acid in solution, the extent of base adsorption is regulated by the acid given to the solution by the hydrolytic adsorption, i.e., by the

---

<sup>1</sup> Loc. Cit.

strength of the acid or hydrogen ion concentrations of the solution. This probably accounts for the higher degree of hydrolytic adsorption with salts of organic acids than with salts of inorganic acids.

6. The adsorption of inorganic salts such as KCl by silica is completely hydrolytic, that is, no KCl as such is adsorbed, neither is Cl ion nor HCl adsorbed.

7. The degree of adsorption is determined not only by the specific properties of adsorbent and adsorbate, but is dependent upon the solubility of solute in the solvent and upon the solid-liquid interfacial tension relationships. If the solubility of a given adsorbate is the same in a series of different solvents, greater adsorption will occur from solutions the solvent of which has the lower adhesion tension with the adsorbent.



## HEAT OF WETTING OF CARBON BY BINARY LIQUID MIXTURES

---

In order to interpret data obtained in a study of heat of wetting of solids by a binary liquid system it is desirable to keep in mind the conditions which may exist during the process of adsorption. When an adsorbent comes into contact with a solution, its surface is exposed to both solvent and solute molecules. Theoretically, one of three things may happen: (1) the solute molecules may be adsorbed exclusively; (2) the solvent molecules may be adsorbed exclusively; or (3) both solute and solvent molecules may be adsorbed. In the latter case preferential adsorption of either solute or solvent may predominate. Suppose the adsorption of A from a binary mixture of A and B be exclusive. So long as there is sufficient A to cover the surface of the adsorbent, none of B will be adsorbed. If, however, one decreases the concentration of A until there is an insufficient amount of it to form a complete monomolecular layer on the surface of the adsorbent, some of B will then be adsorbed. If, on the other hand, both A and B are adsorbed, but to different degrees, the surface of the adsorbent will be covered by both components.

In the study of adsorption from solutions it has been customary to determine merely the change in concentration of the solution and to disregard the adsorption of the solvent, i.e., relative and not absolute adsorption values have been determined. Calculations have been based on the assumption that solute only was adsorbed. Volume changes due to adsorption of solute have been disregarded; this treatment may involve appreciable errors. There is evidence that both solvent and solute are always adsorbed. Bakr and McBain<sup>1</sup> using charcoal as adsorbent with toluene and acetic acid in the vapor phase found that both toluene and acetic acid were adsorbed and concluded that "true sorption of both solvent and solute is in accordance with the conception that toluene and acetic acid can replace each other in the adsorbed film." Attempts to determine absolute adsorption of solute from solutions have been made by Williams,<sup>2</sup> Osaka,<sup>3</sup> and Ostwald and Izaguirre,<sup>4</sup> but no really satisfactory method has been developed.

It is also customary in adsorption studies to disregard the question of fraction of the surface area actually covered by each of the components. It is our belief that information along this line will throw some light on the nature of adsorption and may eventually lead to a method for the determination of absolute adsorption of each component. It was the purpose of this investigation to obtain information bearing upon these problems.

---

<sup>1</sup> J. Am. Chem. Soc., **46**, 2718 (1924).

<sup>2</sup> Medd. K. Vetenskapsakad, Nobel-Inst., **2**, 27 (1913).

<sup>3</sup> Mem. Coll. Sci. Kyoto Univ., **1**, 257 (1915).

<sup>4</sup> Kolloid-Z., **30**, 279 (1922).

It is well known that heat is evolved when a solid is wetted by a liquid. Disregarding the mechanism of wetting and assuming no chemical reaction to occur, it may be stated that the heat of wetting represents the decrease of total surface energy within the system. Since surface tension (or interfacial tension) is numerically equal to the free surface energy per unit area, Helmholtz's equation  $E = S - T \, dS/dT$  may be applied where  $S$  is used to represent either the surface tension of the solid (or free surface energy per unit area) or the interfacial tension of solid against liquid and  $E$  the total surface energy per unit area.

When a solid (say of total area  $a$ ) is immersed in liquid, it is assumed that no external work is done.<sup>1</sup> Suppose we let  $E_1$  represent total surface energy

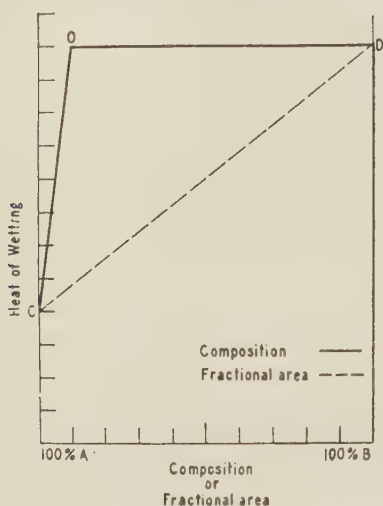


FIG. 1

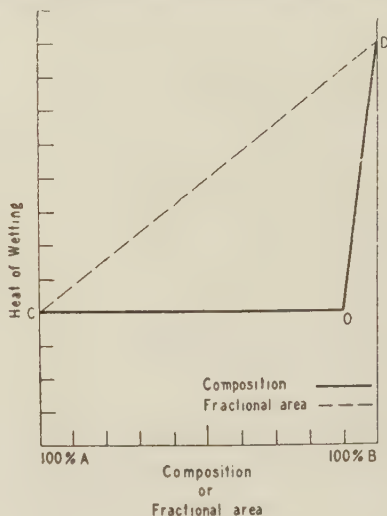


FIG. 2

of the solid and  $E_{12}$  the total interfacial energy of the solid-liquid system. Then, in accordance with the First Law of Thermodynamics, the heat evolved,  $-Q$ , is represented by the following expression:

$$-Q = a(E_1 - E_{12})$$

which in turn is equal to

$$a \left\{ (S_1 - S_{12}) - T \left( \frac{dS_1}{dT} - \frac{dS_{12}}{dT} \right) \right\}$$

where  $S_1$  and  $S_{12}$  refer to surface tension of the solid and interfacial tension of the solid-liquid respectively. Thus the heat of wetting is directly proportional to surface area. Since the interfacial tension values ( $S_{12}$ ) for different liquids against a given solid are different,<sup>2</sup> the degree of wetting of a solid

<sup>1</sup> It will be assumed that, when a solid is immersed in a liquid, the only appreciable energy change which occurs is that due to the substitution of a solid-liquid interface for a solid air interface; that any energy changes due to slight changes in concentration of solution or to the very small volume change within the system are of such a low order that the thermal changes observed are accurate within the limits of experimental error.

<sup>2</sup> Bartell and Osterhof: Colloid Symposium Monograph, 5, (1927).

by different liquids must be different and accordingly the heat of wetting for each of these systems must be different. This has been shown by the work of a number of different investigators.<sup>1</sup>

If both liquids are adsorbed from a binary mixture, the heat evolved must be due to the combined effect of both liquids. Should the wetting be by one component only, the presence of the other component would not appreciably affect the amount of heat evolved until the concentration of the more strongly adsorbed component should fall below a certain limit which corresponds to the formation of a complete monomolecular layer. In case both components are adsorbed, the heat evolved must be different from that evolved if but one is adsorbed. These relations can best be shown in Figs. 1-3.

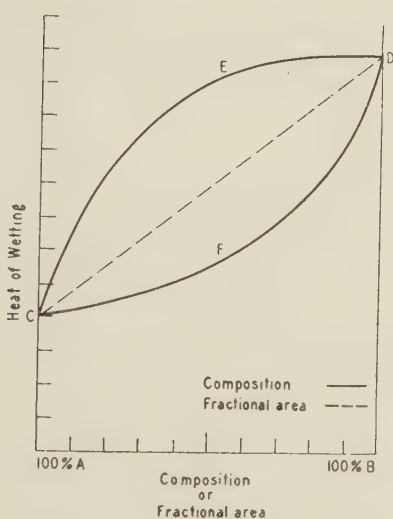


FIG. 3

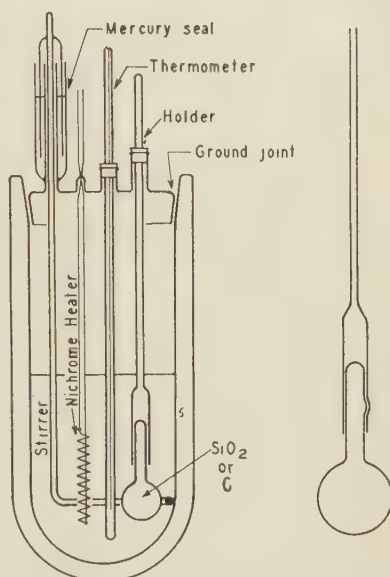


FIG. 4 a and b

Fig. 1 represents the case in which B only is adsorbed. As the concentration of the solution is decreased progressively from 100% B, the heat evolved is the same at each step until there is an insufficient amount of B present to form a monomolecular layer (point O). As the concentration of B is decreased further, the heat of wetting becomes progressively less until point C is reached, which corresponds to the heat of wetting of pure A. Fig. 2 represents the condition in which A is adsorbed exclusively from solution. Curve E of Fig. 3 represents adsorption of both components. B is indicated as being adsorbed preferentially throughout the entire range of concentration, while curve F represents the opposite case, i.e., A is preferentially adsorbed throughout.

If the two components are adsorbed in the same ratio as that of their composition in the solution (i.e., no preferential adsorption) the heat of

<sup>1</sup> Grimm, Raudenbusch and Wolff: *Z. angew. Chem.*, **41**, 104 (1928); Patrick and Grimm: *J. Am. Chem. Soc.*, **43**, 2144 (1921); Gaudechon: *Compt. rend.*, **147**, 209 (1913); Herbst: *Kolloid-Z.*, **38**, 314 (1926); Andress and Berl: *Z. physik. Chem.*, **122**, 81 (1926).



wetting will change linearly with the concentration as is indicated by the dotted line, provided that a molecule of component A occupies the same area on the surface of the adsorbent as a molecule of component B. If the heat of wetting be determined for different concentrations of the solution, and if a horizontal line be drawn from a point on the experimental curve thus obtained to the dotted line, the point of intersection of the horizontal to the dotted line will then represent the ratio of the solid surface occupied by each component when the solution is of the composition given by the point on the experimental curve. The extent of deviation of the experimental curve from the straight line, measured horizontally, gives a relative measure of preferential adsorption at any particular concentration. Thus by measuring the heat of wetting of an adsorbent with solutions of any concentration we should be able to determine the fraction of the surface actually covered by each component, as also the effect of composition of the solution on the relative distribution of the two components on the surface of the adsorbent.<sup>1</sup>

### Experimental

**Materials:** The carbon was prepared from Merck's pure cane sugar by charring it in a platinum dish. After it was charred, the carbon was ground in an agate mortar to a fine powder and heated to 1200°C for twelve hours in the absence of air. This carbon was then heated in a covered alundum thimble with a Meker burner for six hours with a limited supply of air. It was cooled in a desiccator and stored in a weighing bottle. Even though the carbon prepared in this manner might have contained a trace of impurities introduced by the flame rendering it unsuitable for exact work on adsorption of electrolytes, the amount of impurities was not sufficient to invalidate the

<sup>1</sup> In the last two cases (Fig. 3) the situation is complicated by the fact that the surface areas covered by each of the molecules of different molecular species are probably in most cases not identical. Therefore, even though no preferential adsorption were to occur, the change of heat of wetting with composition will not be linear. The deviation of the curve from the straight line depends upon the relative area covered by the molecules (and also upon the difference in the heat of wetting values of the pure liquids). It is to be noted that these curves would never cross the straight line. In the liquids we have used, it is very improbable that the surface area covered by one kind of molecule is much greater than that covered by the other; consequently the actual deviation would not be great. If the experimental (composition-heat of wetting) curve were found to cross the straight line, it is very probable that preferential adsorption of each of the components occurred over some portion of the concentration range even though the point of inversion (i.e., the point of zero adsorption or no preferential adsorption) may not be identical with the point of intersection. A case of extreme preferential adsorption, that of alcohol-nitrobenzene, has been studied by C. K. Sloan of this laboratory, who found that both components were adsorbed by carbon even though the alcohol was much less adsorbed than the nitrobenzene. The concentration corresponding to zero preferential adsorption as determined by him was found to be very close to the concentration representing the point of intersection of the heat of wetting-composition curve with the dotted line. Therefore, the deviation of the actual (composition-heat of wetting curve in case of no preferential adsorption) curve from the straight line must be slight and for practical purposes we may consider the two curves identical. Unless the exact area occupied by the molecules of each component is known, such curves will only give a *qualitative* indication of preferential adsorption and can not be considered as representing a quantitative measurement. (The restriction made above will, however, not invalidate our discussion). Rigorously, the straight line in the figure represents the change in the distribution of the solid surface between the two liquids, whether or not the molecules of the one occupies the same area as the molecules of the other.

heat of wetting data. All liquids were purified by standard methods. The dilute solutions were made up by weight and the concentrated ones by volume.

Apparatus and method: The calorimeter used in this work was a Dewar flask with fittings similar to those used by Patrick and Grimm<sup>1</sup> (Fig. 4a). The cover of the flask was gas tight. Both the Beckmann thermometer and the heating coil were cemented into the cover with DeKhotinsky cement.

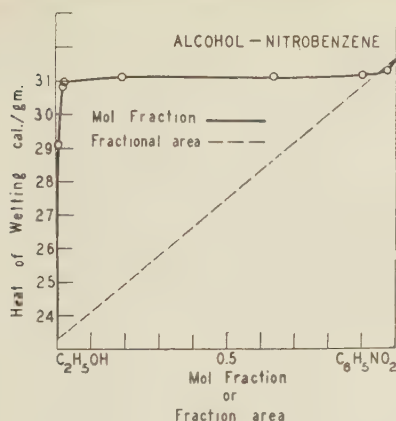


FIG. 5

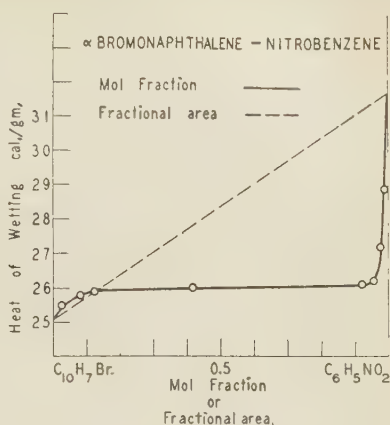


FIG. 6

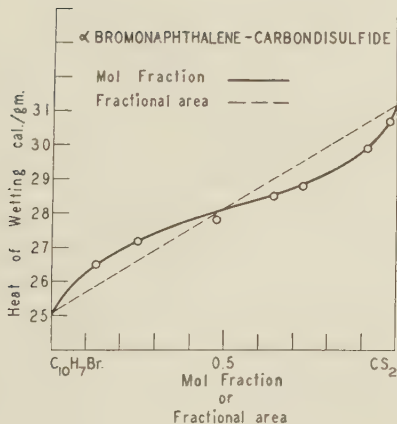


FIG. 7

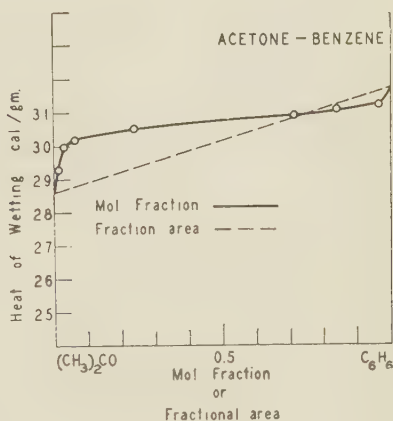


FIG. 8

The stirrer was mercury sealed. When the bulb containing the solid was set in position, the whole system was gas-tight; no evaporation was detected over a six-hour period. The carbon powder was sealed in a thin walled glass bulb which in turn was sealed to a glass holder (Fig. 4b). After the bulb had been introduced, the whole apparatus was placed in a felt jacket. The liquid was stirred continuously until the temperature remained constant for at least twenty minutes. This procedure is important; otherwise it is very dif-

<sup>1</sup> J. Am. Chem. Soc., **43**, 2144 (1921).

ficult to obtain uniform results. The bulb was then broken by pushing it gently against the wall of the calorimeter, and the change in temperature was noted. Just before the bulb was broken, the temperature external to the calorimeter was raised slightly (about  $0.5^{\circ}\text{C}$ ) so that the temperature of the liquid after wetting and that of the surroundings was the same, heat loss was thus minimized. With some practice it was possible to maintain the temperature within the calorimeter (after wetting) constant for at least ten

TABLE I  
Heat of Wetting of Carbon with Binary Mixtures

1. Benzene-Acetone

| Mole percent<br>of $\text{C}_6\text{H}_6$ | Heat per<br>gm. carbon |
|-------------------------------------------|------------------------|
| 0.0                                       | 28.6 cal               |
| 1.48                                      | 29.3                   |
| 3.00                                      | 30.0                   |
| 6.06                                      | 30.2                   |
| 23.62                                     | 30.5                   |
| 71.4                                      | 30.9                   |
| 84.1                                      | 31.0                   |
| 96.6                                      | 31.2                   |
| 100                                       | 32.7                   |

3.  $\alpha$ -Bromonaphthalene-  
Carlson disulphide

| Mole percent<br>of $\text{CS}_2$ | Heat per<br>gm. carbon |
|----------------------------------|------------------------|
| 0.0                              | 25.1                   |
| 12.8                             | 26.5                   |
| 25.2                             | 27.2                   |
| 47.6                             | 27.8                   |
| 64.4                             | 28.5                   |
| 72.8                             | 28.8                   |
| 91.5                             | 29.9                   |
| 98.0                             | 30.7                   |
| 100                              | 31.2                   |

2. Alcohol-Nitrobenzene

| Mole percent<br>of alcohol | Heat per<br>gm. carbon |
|----------------------------|------------------------|
| 0.0                        | 31.7 cal               |
| 2.6                        | 31.3                   |
| 10.0                       | 31.2                   |
| 36.2                       | 31.1                   |
| 80.7                       | 30.9                   |
| 98.1                       | 30.8                   |
| 99.5                       | 29.1                   |
| 99.7                       | 27.8                   |
| 99.8                       | 26.5                   |
| 100                        | 23.3                   |

4.  $\alpha$ -Bromonaphthalene-  
Nitrobenzene

| Mole percent<br>of nitrobenzene | Heat per<br>gm. carbon |
|---------------------------------|------------------------|
| 0.0                             | 25.1                   |
| 2.7                             | 25.5                   |
| 8.1                             | 25.8                   |
| 12.3                            | 25.9                   |
| 41.8                            | 26.0                   |
| 92.3                            | 26.1                   |
| 96.0                            | 26.2                   |
| 97.8                            | 27.2                   |
| 99.0                            | 28.9                   |
| 100                             | 31.7                   |

minutes. In all cases the calorimeter temperature reached the maximum within two minutes after the bulb was broken and remained constant for five or six minutes. This temperature reading was taken as the final reading. The heat capacity of the calorimeter together with that of the solid was determined by adding a definite amount of electrical energy to the system and noting the temperature rise. In some cases no attempt was made to equalize the calorimeter and room temperatures, but instead, thermometer readings



were taken at fifteen second intervals, and corrections for heat loss were made by applying White's<sup>1</sup> formula. The two methods gave close agreement. In order to make sure that no evaporation of liquid occurred, the heat capacity of the system was determined at two hour intervals. Identical results were obtained in every case.

The results for four binary liquid systems are given in Table I, and are plotted in Figs. 5-8.

### Discussion

From the data obtained two interesting facts are noted. The first is that neither component is adsorbed exclusively at any concentration, and the second is that "positive" adsorption of each liquid occurs over a certain range in each of the systems, the degree of adsorption of each component being dependent upon the concentration of the solution.<sup>2</sup> It thus follows that the usual method of measuring amount of adsorbed solute is not strictly accurate since the usual assumption regarding the non-adsorption of the solvent is not justified. It is also evident that the determination of surface area of adsorbents by adsorption experiments, as used by Paneth and Vorwerk,<sup>3</sup> Paneth and Radu,<sup>4</sup> and Garner, Knight and McKie<sup>5</sup> will most probably give low values, even in those cases where the adsorption is not affected by the hydrogen ion concentration of the solution, because allowance was not made for the adsorption of the solvent.

If it be considered that surface tension, or interfacial tension, is the determining factor in adsorption, and if Gibbs' theorem can be rigidly applied to solid-liquid interfaces, we have for a system containing an ideal solution,

$$u_1 = - (dS_{12}/dF_1) = - 1/RT dS_{12}/d\log c_1$$

where  $u_1$  is the excess of component 1 at the interface,  $F_1$  is the chemical potential of component 1 and  $c_1$  its concentration in the bulk of the solution. Since the adhesion tension  $A$  is given by the equation

$$A_{12} = S_1 - S_{12}$$

we have at constant temperature,

$$dA_{12} = - dS_{12}$$

as the surface tension of the solid  $S_1$  is a function of temperature only. The formulation

$$u_1 = 1/RT dA_{12}/d\log c_1$$

expresses then the relation of adhesion tension to adsorption,<sup>6</sup> that is, the constituent which raises the adhesion tension of the solution against the

<sup>1</sup> J. Am. Chem. Soc., **48**, 1147 (1926).

<sup>2</sup> This conclusion has since been confirmed by adsorption experiments carried out in this laboratory by the interferometric method.

<sup>3</sup> Z. physik. Chem., **101**, 445 (1922).

<sup>4</sup> Ber., **57**, 1221 (1924).

<sup>5</sup> J. Phys. Chem., **31**, 641 (1927).

<sup>6</sup> Bartell and Sloan: J. Am. Chem. Soc., **51**, 1643 (1929).

solid will be positively adsorbed. It is well known<sup>1</sup> that for many solutions the concentration-surface tension curve has a minimum point. By analogy, it is reasonable to expect the interfacial tension curve for solid-liquid systems to exhibit a similar relationship. Likewise, a maximum point in the adhesion tension concentration curve might be expected. It follows then that positive adsorption of both components may take place. It was found experimentally,<sup>2</sup> however, that in some systems which showed "positive" adsorption of both components, no maximum point existed on the adhesion tension-concentration curve. Letting  $c$  represent the concentration of the component with the higher adhesion tension,  $dA_{12}/d\log c$  was found to be always positive.<sup>3</sup> As both  $R$  and  $T$  are positive quantities,  $u_1$  should necessarily be positive throughout the whole range of concentration. This was found to be contrary to fact. It thus follows that adsorption of liquids from a binary mixture on a solid surface can not be completely accounted for by the interfacial tension-concentration relationships alone. It should be remarked, however, that this is not a conclusive proof of the inapplicability of Gibbs' theorem as related to solid-liquid interfaces. It is well known that if a substance raises the surface tension of the solvent, the increase is usually very small. If a similar action occurs at a solid-liquid interface, the effect of the component with lower adhesion tension may be small when compared with that of the one having a higher adhesion tension. The method available at present for the measurement of adhesion tension may not be sufficiently accurate to detect the small increase of adhesion tension due to the addition of a second component, (but this is not believed to be the case.) Work is being conducted in this laboratory which will permit of more detailed discussion of this point later.

The above apparent anomaly, can however, be accounted for in another manner. For the sake of simplicity the process of adsorption from binary mixtures may be treated by the following thermodynamically identical process. Let the adsorbent be first added to the pure liquid A, and after equilibrium has been established, a small amount of liquid B, which has a lower adhesion tension against the solid than A, be added to the system. Liquid B will then displace a small amount of A from the solid surface and equilibrium will again be reached. The free energy changes accompanying the whole process are as follows:

<sup>1</sup> Whatmough: *Z. physik. Chem.*, **39**, 129 (1902).

<sup>2</sup> Bartell and Miller: unpublished results.

<sup>3</sup> The adhesion tension values of the liquids used, against carbon, are approximately as follows:

|                            |   |      |                             |
|----------------------------|---|------|-----------------------------|
| Carbon disulphide          | = | 89.5 | Bartell and Osterhof        |
| $\alpha$ -Bromonaphthalene | = | 89.2 | " "                         |
| Benzene                    | = | 81.1 | " "                         |
| Nitrobenzene               | = | 78.7 | " " unpublished             |
| Acetone                    | = | 71.0 | Bartell and Fu, unpublished |
| Alcohol                    | = | 56.5 | " " unpublished             |
| Water                      | = | 54.7 | Bartell and Osterhof        |

When the solid is wetted by liquid A, the solid surface,  $a$ , with a surface tension  $S_1$ , is replaced by an equal interface of interfacial tension  $S_{12}$ . The change in free energy at constant temperature and pressure is represented by

$$\int dF = a \int_{S_1}^{S_{12}} dS = a(S_{12} - S_1) = -a A_{(s-A)}$$

where  $A_{(s-A)}$  is the adhesion tension of A against the solid. Suppose a small amount of B is then added. Adsorption occurs in finite time. At zero time, that is before the adsorption takes place, the concentration of A is  $c_2$  and that of B is  $c_1$ . After adsorption, the concentrations are  $c_2'$  and  $c_1'$  respectively. We have then  $c_2' > c_2$ , and  $c_1' \ll c_1$ . The free energy change due to change in concentration is as follows:

$$\Delta F = \Delta F_A + \Delta F_B$$

where  $\Delta F_B$  is the free energy change due to change in concentration of solution as a result of adsorption of B, and  $\Delta F_A$  is that due to the desorption of A. As the process of adsorption involves a change in concentration of the solution, the change in free energy is represented by

$$\int_1^2 dF = \int_{P_1}^{P_2} v dp$$

where  $v$  is the volume and  $P$  the osmotic pressure of the solution. From this it follows<sup>1</sup>

$$\Delta F_B = \int_{P_1}^{P_1'} v dP = \frac{n}{N} RT \log_e \frac{c_1'}{c_1}$$

which is a negative quantity ( $n$  is the number of molecules of B removed from solution by adsorption). In a similar manner

$$\Delta F_A = \frac{n'}{N} RT \log_e \frac{c_2'}{c_2}$$

which is positive. It is not to be considered that  $n$  and  $n'$  (the number of molecules of A restored to the solution) are identical unless the area occupied by a molecule of A is exactly the same as that occupied by a molecule of B.

Since  $c_1$ , the concentration of B, is very small at the start, a slight adsorption will correspond to a large relative change in concentration of B, while the concentration of A remains practically constant; consequently there is decided decrease in free energy due to the adsorption of B. When B displaces A from the surface there is a change in free surface energy, as the adhesion tensions of A and B are not the same. The decrease of free energy due to the adsorption of B is  $(a'A_{s-B})$ , and the increase due to the adsorption of A is  $(a'A_{s-A})$ , where  $a'$  is the area on the adsorbent which was formerly occupied by A but is now taken up by B and  $(A_{s-B})$  and  $(A_{s-A})$  are the adhesion tensions of B and A respectively. The total change in free

<sup>1</sup> For this treatment it is assumed that the solution is ideal, otherwise activity values should be used in place of concentration values.



surface energy is of course the algebraic sum of the two changes. If, as we have assumed,  $(A_{s-A})$  is greater than  $(A_{s-B})$ , there is an increase in free surface energy due to the adsorption of B. Since the adsorption of a liquid of low adhesion tension from another of high adhesion tension is generally very slight,<sup>1</sup> this increase in free surface energy is small. Hence, it appears that a net decrease in free energy will result due to the different steps occasioned by the process of adsorption. It was found<sup>2</sup> that the adsorption of the component with low adhesion tension, B in the case in question, from A follows the Freundlich's equation. It follows, then, that at higher concentrations more B will be adsorbed than if but a trace of it were present. As one increases the concentration of B, the free energy decrease due to dilution of B through adsorption of it will become smaller and smaller, while on the other hand, the increase of free energy due to displacement of A becomes relatively greater. When these two quantities become of the same magnitude there will be no preferential adsorption of either component, i.e. the relative concentration on the surface of the adsorbent will be the same as that in the bulk of the solution. This is represented on the curves by the point where the experimental curve intersects the dotted line. If the concentration of B is further increased, the decrease in free energy due to dilution becomes smaller than the increase due to displacement. Hence, B will not displace A from the surface, and A will be preferentially adsorbed.

These curves also show that even though a liquid with low adhesion tension can displace one with higher adhesion tension, the adsorption of the former is usually very slight. If the two components have nearly the same adhesion tension, such as carbon disulfide and alpha bromonaphthalene, the preferential adsorption is low.

It is generally believed that heat of wetting is a measure of adsorbability. Berl and Wachendorff<sup>3</sup> concluded that less adsorption will occur from those solutions the solvent of which has a high heat of wetting, as the high adsorption of the one component will greatly decrease the adsorption of the other. Grimm, Raudenbusch and Wolff,<sup>4</sup> from a study of the heat of wetting of silica by alcohol-carbontetrachloride mixtures, also concluded the liquids showing a higher heat of wetting are more strongly adsorbed. While this generalization is true in most cases, it is by no means universal. Alphabromonaphthalene gives a comparatively low heat of wetting with carbon, but it is strongly adsorbed from nitrobenzene which has a much higher heat of wetting. This is really not surprising since the heat of wetting is a measure of the total surface energy change and not the free surface energy change. The latter is measured by the adhesion tension and this value for alphabromonaphthalene against carbon is high.

The curves tend to confirm the view expressed by Firth and Purse<sup>5</sup> that water in silica gel can be completely displaced by alcohol. Even though the

<sup>1</sup> Bartell and Sloan: J. Am. Chem. Soc., **51**, 1643 (1929).

<sup>2</sup> Bartell and Sloan: J. Am. Chem. Soc., **51**, 1637 (1929).

<sup>3</sup> Kolloid-Z., **36**, (Zsigmondy Festschrift) 36 (1925).

<sup>4</sup> Z. angew. Chem., **41**, 104 (1928).

<sup>5</sup> J. Phys. Chem., **30**, 617 (1926).

adhesion tension of alcohol against silica cannot be determined directly, the calculated value was found by us to be only a few dynes lower than that of water. As the two adhesion tensions approach each other, no one component will be predominantly adsorbed. If pure alcohol be continuously added and decanted off there is no reason to expect (from the present data) that the last trace of water cannot be completely displaced.

### Summary

1. The heat of wetting of carbon with binary liquid mixtures has been determined with four different binary liquid systems.

2. A method has been proposed for the determination of the fractional part of total surface of adsorbent possessed by each of the two components.

3. It was found that in no case was either one of the liquids in a given system "exclusively" adsorbed. The component with the higher adhesion tension was adsorbed preferentially over a wide range of concentration while the component with the lower adhesion tension was preferentially adsorbed only at low concentrations, in small amounts, and over but a narrow concentration range.

4. The applicability of Gibbs adsorption theorem to solid liquid interfaces has been discussed and one of the discrepancies between theory and fact pointed out.

5. The thermodynamical relations which must exist in the process of displacement from the adsorbed state of one liquid by another were presented.

6. The general relationship which exists between heat of wetting and adsorption was discussed.

*Chemical Laboratory  
University of Michigan  
Ann Arbor, Michigan*









